12804

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(12) (19) (CA) **Demande-Application**

(21) (A1) **2,281,405**
(22) 1999/09/02
(43) 2000/03/02

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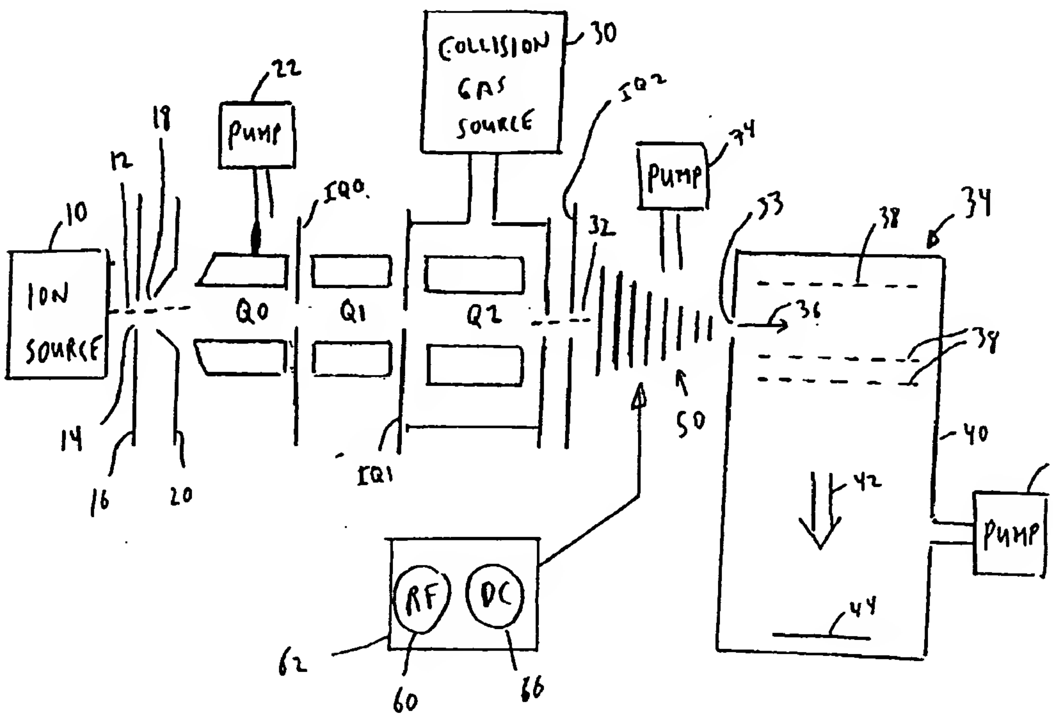
(51) Int.Cl.^{6} H01J 49/40
(30) 1998/09/02 (60/099,064) US

(54) **SPECTROMETRE DE MASSE AVEC SYSTEME CONIQUE DE GUIDAGE DES IONS**

(54) **MASS SPECTROMETER WITH TAPERED ION GUIDE**



(57) A mass spectrometer system in which an ion beam from a collision cell, mass analyzer or other ion transmission device is directed into an ion guide formed by a set of spaced part conductive rings, for transmission into a TOF analyzer. The ion guide tapers in height from its entrance to its exit, so that the ion beam is reconfigured into a flat thin sheet of charge having a reduced height and increased width as compared with the original ion beam. The decrease in height reduces spacial dispersion of the ions, increasing the resolution of the TOF, while the increase in width decreases space charge effects, and increases detector dynamic range. Fragmentation of the ions can also be performed in the ion guide, removing the need for a separate collision cell.

ABSTRACT OF THE DISCLOSURE

A mass spectrometer system in which an ion beam from a collision cell, mass analyzer or other ion transmission device is directed into an ion guide formed by a set of spaced part conductive rings, for transmission into a TOF analyzer. The ion guide tapers in height from its entrance to its exit, so that the ion beam is reconfigured into a flat thin sheet of charge having a reduced height and increased width as compared with the original ion beam. The decrease in height reduces spacial dispersion of the ions, increasing the resolution of the TOF, while the increase in width decreases space charge effects, and increases detector dynamic range. Fragmentation of the ions can also be performed in the ion guide, removing the need for a separate collision cell.

BP #571-580

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<u>CANADA</u>

<u>Title</u>: MASS SPECTROMETER WITH TAPERED ION GUIDE

<u>Inventor(s)</u>: Charles Jolliffe, Bruce Thomson

Title: MASS SPECTROMETER WITH TAPERED ION GUIDE

FIELD OF THE INVENTION

This invention relates to a mass spectrometer system having a tapered ion guide for producing a flat thin sheet of charge suitable for introduction into a mass analyzer such as a time of flight (TOF) instrument.

BACKGROUND OF THE INVENTION

TOF mass analyzers have existed for many years and are noted for their high resolution. However for optimum results, they require an input ion beam in which the initial conditions, namely the start time, location and energy of the ions, have minimum dispersion. If the ions introduced into the TOF analyzer are, for example, dispersed spatially, then the resolution will suffer.

It has become common practice to introduce ions into a TOF analyzer using the method of orthogonal extraction from a quadrupole or tandem mass spectrometer, such as the collision cell of a tandem mass spectrometer. Unfortunately, the ion beam from the collision cell of a conventional mass spectrometer has a relatively large diameter, typically about 2 mm. The spatial dispersion inherent in this beam adversely affects the resolution of a following TOF analyzer. It is difficult to reduce the spatial dispersion, and doing so tends to increase space charge effects, which also adversely impact the performance of the instrument.

BRIEF SUMMARY OF THE INVENTION

It is therefore an object of the invention to provide an ion guide which will accept an ion beam from a preceding stage and will reduce the diameter of the ion beam while spreading it out, to produce a relatively flat, thin, sheet of charge which is more suited for introduction into an orthogonal extraction TOF instrument.

In one of its aspects the invention provides a method of operating a mass spectrometer system having a time of flight (TOF) analyzer having an ion extraction region and a flight tube, comprising: providing ions to be analyzed, and passing said ions through a tapered ion guide to configure the shape of the volume occupied by said ions into a substantially flat thin sheet of ions, directing said flat thin sheet of ions into said extraction region of said TOF analyzer, and extracting said flat thin sheet of ions in a direction substantially orthogonal to the plane of said flat thin sheet of ions into said flight tube of said TOF analyzer.

In another aspect the invention provides a mass spectrometer system comprising a time of flight (TOF) analyzer, and an ion guide for introducing ions into said TOF analyzer along a path of travel, said ion guide tapering in height in the direction of said path of travel so that ions entering or located in said ion guide are configured into a volume in the form of a substantially flat thin sheet, and an ion transmission path for conducting said flat thin sheet of ions into said TOF analyzer.

Further aspects and advantages of the invention will appear from the following description, taken together with the accompanying drawings.

BRIEF SUMMARY OF THE DRAWINGS

In the drawings:

Fig. 1 is a schematic view of a mass spectrometer system incorporating an ion guide according to the invention;

Fig. 2 is a diagrammatic perspective view of an ion guide according to the invention;

Fig. 3 is a diagrammatic view showing the path of an ion in an ion guide according to the invention; and

Fig. 4 is a side sectional view showing a portion of an ion guide according to the invention, constructed from printed circuit boards;

Fig. 5 is a diagrammatic end view of the ion guide of Fig. 4; and

Fig. 6 is a diagrammatic view of a modified mass analyzer system according to the invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Reference is first made to Fig. 1, which shows a conventional ion source 10 which supplies ions 12 along a path of travel through an aperture 14 in an aperture plate 16, through a skimmer opening 18 in a skimmer 20, into an RF-only ion transmission quadrupole Q0 in a chamber evacuated by pump 22.

The ions 12 pass through Q0, and through a lens IQ0 into a resolving quadrupole Q1 (also in an evacuated chamber) where ions of a desired mass to charge ratio are selected, and undesired ions are rejected radially. From quadrupole Q1 the selected ions pass through lens IQ1 into a collision cell Q2 supplied with collision gas from source 30. In quadrupole Q2 the ions (referred to as parent ions) are fragmented to produce daughter ions. (It is assumed in this disclosure that the parent ions are injected into Q2 with sufficient kinetic energy to fragment.) The daughter ions leave Q2 axially and passes through lens IQ2 in an ion beam 32 which is typically about 2 mm in diameter, together with gas from Q2 (since Q2 is at the relatively high pressure of about 5 millitorr). The arrangement so far described is entirely conventional and is well known.

It would normally be desired next to introduce the ion beam 32 into inlet 33 of a TOF analyzer 34. In TOF 34, the ion beam is extracted orthogonally to its path of travel 36, by extraction electrodes 38. Thus, ions from ion beam 32 are pulsed sideways down the flight tube 40, in the direction of arrow 42, to a detector 44 where they are detected for analysis. Flight tube 40 is evacuated by pump 46.

According to the invention, a tapered ion guide 50 is inserted between Q2 (or lens IQ2) and the inlet 33 of TOF 34. The tapered ion guide 50 may comprise (as shown in Fig. 2) a set of rectangular lenses or rings 52-1 to 52-8 inclusive, i.e. each lens or ring has a rectangular opening.

While the lenses could be formed from wire, more commonly they will be formed conventionally from metal plates each having a rectangular hole therein. Ring 52-1 serves as an inlet ring while 52-8 serves as an exit ring. The number of rings may of course vary and will commonly be greater than that shown.

It will be seen that the height of the ion guide rings decreases or tapers from the entrance ring 52-1 to the exit ring 52-8. The decrease in height may be linear as shown, or may be of other geometric form to produce the best results.

In addition, as the rings 52-1 to 52-8 taper in height, they also increase outwardly in width from the entrance ring 52-1 to the exit ring 52-8, as also shown in Fig. 2.

RF from an RF supply 60 (which forms part of an RF and DC source 62) is applied to the rings 52-1 to 52-8, with alternating poles 60A, 60B of the RF supply 60 connected to each alternate ring as shown in Fig. 2. Therefore, one pole 60A is connected (through capacitors C) to rings 52-1, 52-3, 52-5 and 52-7, while the other pole 60B is connected through further capacitors C to rings 52-2, 52-4, 52-6 and 52-8. This produces what is seen by the ions to be an alternating RF field as the ions travel through the rings from one end to the other. Ion guides consisting of a stack of spaced rings with RF and/or DC connected thereto are known and are described for example in an article entitled "Stacked-Ring Electrostatic Ion Guide" by Guan and Marshall, 1996 J Am Soc Mass Spectrum 1996, pages 101-106, and in the article entitled "A Novel Ion Funnel for Focusing Ions at Elevated Pressure Using Electrospray Ionization Mass Spectrometry", by Richard Smith et al., Rapid Comm. Mass Spectrom. 11, 1813-1817 (1997).

To ensure that the ions will continue moving through the ion guide 50, a small DC drag field is provided, produced by DC potentials V1 to V8 applied respectively to the rings. Each DC potential V2 to V8 is slightly higher than the preceding potential (typically at a gradient of about 10 volts per meter). Potentials V1 to V8 are obtained from DC supply 66, which forms part of source 62.

As ions enter the ion guide 50, they tend to follow a path such as that shown at 70 in Fig. 3. The path 70 is not sinusoidal, but rather is more like that of the path of a bouncing ball, being reflected back and forth along the path of travel until, at the exit ring 52-8 the amplitude of the path becomes very small and the frequency of oscillations become higher. To deal with this path, the spacing along the length of the path of travel between the rings is made smaller in the direction of the ion movement, so that the rings become closer together at the exit end of the ion guide 50.

As the ions are squeezed in one dimension, and spread out in the other dimensions, from a beam into a shape approximating a thin sheet, the ion temperature tends to increase, by a factor of as much as three. However the presence of gas within the ion guide tends to cool the ions by collisional damping, reducing the ion temperature. This is so even though much of the gas is removed from the ion guide 50 by pump 74, so that minimal gas will enter the TOF analyzer 34.

In addition, although the ion beam is squeezed in height, it is as mentioned allowed to expand widthwise in direction W, as the width of the rings 52-1 to 52-8 increases. Thus, space charge effects which would otherwise occur are minimized, and the cylinder ion beam is transformed to have a shape which is generally that of a wide, flat, thin sheet of charge. Such a sheet of charge is more suited to being extracted into the flight tube 40 of the TOF analyzer 34.

It is found, when a tapered ion guide of the kind shown is used, that the ion beam can be reduced in height from 2 mm to approximately .2 mm, or a ten times improvement, resulting in an increase in resolution in the TOF. The width W of the ion sheet can be as desired, but may for example be 40 mm in the case where the diameter of flight tube 40 is 228 mm. The dimensions of inlet 33 of TOF 34 will of course be made generally rectangular and of a size to admit the sheet of charge.

Although the ion guide rings 52-1 to 52-8 have been shown as increasing in width from the entrance to the exit of the ion guide, if

desired they can all be of equal widths, namely the width of the exit ring 52-8. The ion beam 32 will then simply expand widthwise to fill the space available. However the height will still taper from the entrance to the exit end of the ion guide 50, to transform the ion beam into a flat, thin sheet of charge.

An advantage of spreading the ion beam over this essentially larger area perpendicular to the axis of the TOF instrument is that the ions then more uniformly cover the area of the detector. For example, it is common to use a detector area of up to about 40 mm in diameter. In such cases it is useful to increase the beam width (i.e. to produce a sheet of charge) which is about 40 mm in width, in order to spread the beam across the surface of the detector and avoid local saturation effects on the detector. This helps to increase the dynamic range of the detector.

It can also be advantageous to tailor the gas density along the tapered ion guide in the direction of ion motion, which is possible provided that the ion guide is partially enclosed. With a lower gas density, a lower axial field is required to ensure continued movement of the ions, and a lower axial field is generally helpful because it reduces the energy involved in ion collisions with neutrals, thus reducing ion heating, particularly in the extraction direction. In practice, the gas pressure can be reduced near the exit end of the ion guide, after the ion beam has been reshaped into a thin sheet and the ions have been cooled by collisional damping. Once that has occurred, the gas within the ion guide is less important and can be removed (e.g. by increased ventilation between the ion guide rings). In that case, the axial field between the ion guide rings or lenses can also be made non-uniform, e.g. it can be reduced toward the exit end of the guide where there is less gas and where therefore a smaller axial field is needed to assist movement of the ions through the guide.

While separate rings have been shown, if desired, and as indicated diagrammatically in Fig. 4, printed circuit boards 82, 84 can be used, with circuit tracks 86, 88 laid on them to form the equivalent, electrically, of the rings 52-1 to 52-8. Four such printed circuit board

elements will be used, one for each of the top, bottom and each side of the ion guide, as shown diagrammatically in Fig. 5 where the printed circuit boards at the sides of the guide are indicated at 90, 92 respectively, with circuit tracks 94 shown on the board 90 in Fig. 4. (More than four printed circuit boards can be used if desired, to produce a guide having at least at its entrance a non-rectangular cross-section.) The circuit tracks on each printed circuit board are connected together by any desired means, e.g. by separate connector pieces (not shown) joining each pair of printed circuit boards together. Any other conventional connecting means may also be used. An appropriate opening or set of openings 96 is provided at least in the upper printed circuit board 82 to allow gas in the ion guide to be withdrawn by pump 74.

If desired, in the arrangement of Fig. 1 Q2 can be eliminated and ions from Q1 can be injected directly into the ion guide 50, with sufficient energy to fragment them as indicated in Fig. 6. Collision gas from source 30 is injected into ion guide 50 near its inlet end, as shown. The gas is removed either by a pump (not shown) between the outlet of ion guide 50 and the inlet 33 of the TOF 34, or by providing a separate pump 102 to exhaust the extraction region of TOF 34. The advantage of this arrangement is that as the daughter ions are formed in the ion guide 50 (which acts as a collision cell), they are also reconfigured into a flat thin sheet of charge by the ion guide 50, thus eliminating the need for one component (namely Q2) of the mass spectrometer system.

When printed circuit boards are used to form the ion guide as shown in Figs. 4 and 5, the surface of the printed circuit boards between circuit tracks may normally be made weakly conducting to prevent charging of the surface of the boards.

While the ion beam processed by the tapered ion guide 50 has been shown as originating from a collision cell, or from a mass analyzer with fragmentation to be performed in ion guide 50, it will be realized that the tapered ion guide 50 can be used to reconfigure an ion beam from any ion source or the like into a flat thin sheet of charge suitable for entry into

a TOF analyzer.

While preferred embodiments of the invention have been described, it will be appreciated that various changes may be made within the scope of the invention.

WE CLAIM:

1. A method of operating a mass spectrometer system having a time of flight (TOF) analyzer having an ion extraction region and a flight tube, comprising: providing ions to be analyzed, and passing said ions through a tapered ion guide to configure the shape of the volume occupied by said ions into a substantially flat thin sheet of ions, directing said flat thin sheet of ions into said extraction region of said TOF analyzer, and extracting said flat thin sheet of ions in a direction substantially orthogonal to the plane of said flat thin sheet of ions into said flight tube of said TOF analyzer.

2. A method according to claim 1 and including injecting parent ions into said ion guide while providing a collision gas in said ion guide to fragment said parent ions to produce daughter ions, said flat thin sheet of ions comprising said daughter ions.

3. A method according to claim 1 wherein said ion guide includes an entrance and an exit, and including the step of injecting a cooling gas into said entrance to collisionally cool ions passing through said guide.

4. A method according to claim 3 wherein the density of said cooling gas is lower adjacent said exit than adjacent said entrance.

5. A method according to claim 4 wherein said ion guide includes a longitudinal axis, and including the step of providing an axial electric field along said axis to assist the movement of said ions through said ion guide.

6. A method according to claim 5 wherein said axial electric field is lower adjacent said exit of said ion guide than adjacent said

entrance of said ion guide.

7. A mass spectrometer system comprising a time of flight (TOF) analyzer, and an ion guide for introducing ions into said TOF analyzer along a path of travel, said ion guide tapering in height in the direction of said path of travel so that ions entering or located in said ion guide are configured into a volume in the form of a substantially flat thin sheet, and an ion transmission path for conducting said flat thin sheet of ions into said TOF analyzer.

8. A system according to claim 7 wherein said ion guide comprises a plurality of conductors, each forming a conductive ring around said path of travel, the height of said rings decreasing in the direction of said path of travel.

9. A system according to claim 8 wherein the width of said rings increases in the direction of said path of travel.

10. A system according to claim 8 and including a DC voltage source for applying a small DC drag potential to said rings to establish a DC electric field gradient along said ion guide, to maintain movement of said ions along said ion guide.

11. A system according to claim 8 wherein said rings are formed by wires.

12. A system according to claim 8 wherein said rings are formed by conductive tracks on printed circuit boards.

13. A system according to claim 7 and including a source for injecting collisional cooling gas into said ion guide, to collisionally cool ions passing through said ion guide.

14. A system according to claim 7 and including a collision gas source for injecting collision gas into said ion guide, so that ions in said ion guide may be collisionally disassociated to form daughter ions, and so that said daughter ions may be extracted in the form of said flat thin sheet into said TOF analyzer.

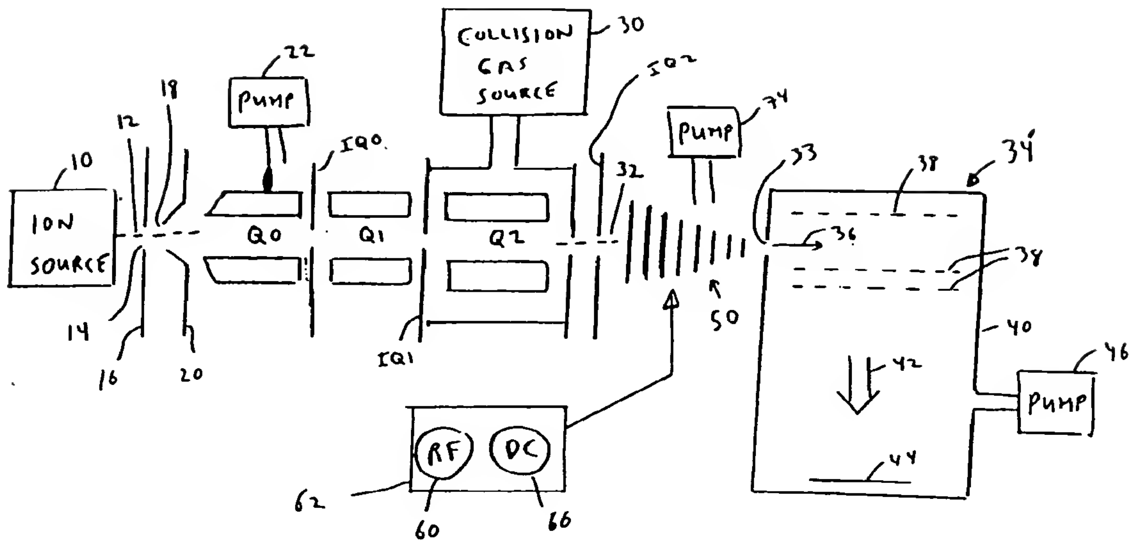

Fig 1

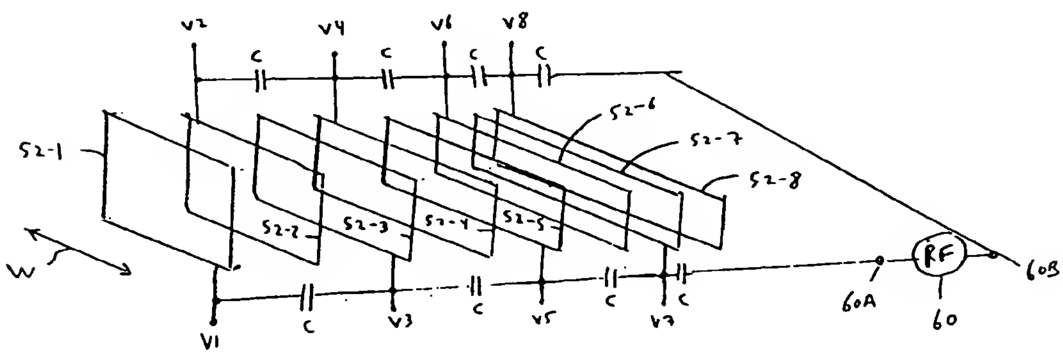

Fig. 2

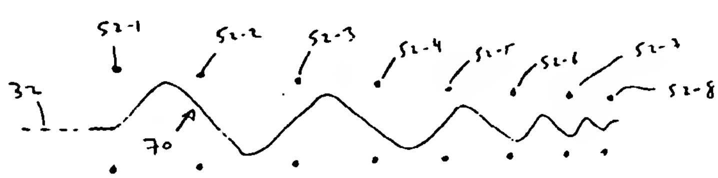

Fig. 3

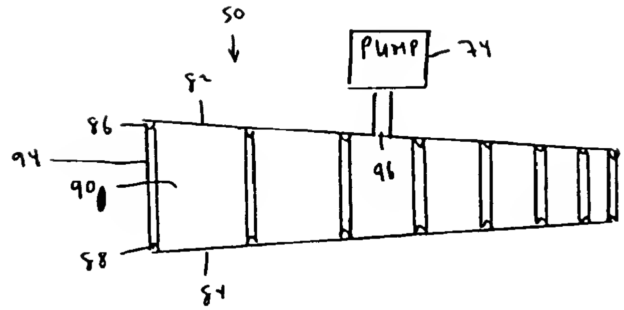

Fig. 4

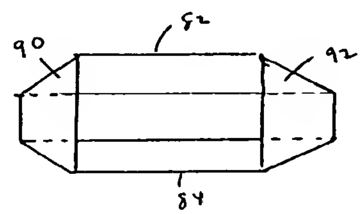

Fig. 5

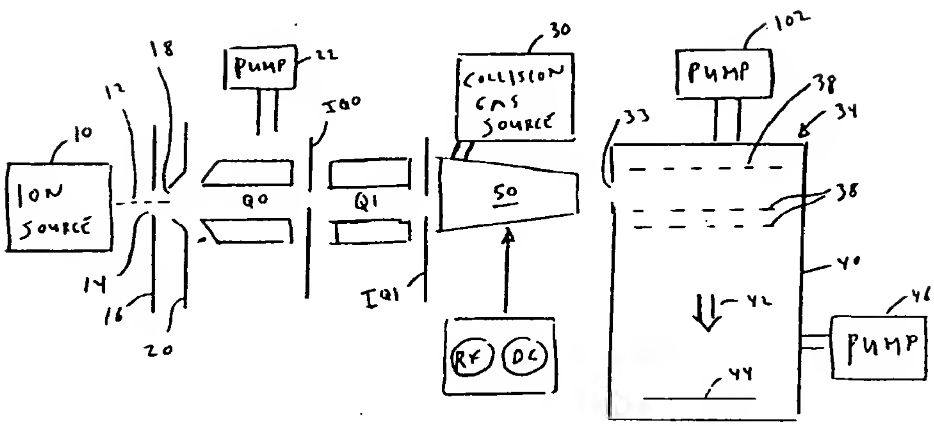

Fig. 6